

Figure 6-5. Service Station Vapor Balance System

Source: Reference 160.

decreases evaporative loss. Installing an internal floating roof in a fixed-roof tank can reduce total emissions by 68.5 to 97.8 percent.¹⁶⁰

For external floating-roof tanks, no control measures have been identified for controlling withdrawal losses and emissions.¹⁶⁰ These emissions are functions of the turnover rate of the tank and the characteristics of the tank shell. Rim seal losses in external floating roof tanks depend on the type of seal. Liquid-mounted seals are more effective than vapor-mounted seals in reducing rim seal losses. Metallic shoe seals are more effective than vapor-mounted seals but less effective than liquid-mounted seals.¹⁶⁰

For additional information on control technology for storage tanks refer to the EPA documents *Compilation of Air Pollutant Emission Factors* (AP-42), Chapter 7³³ and Reference 158.

6.4.7 Control Technology for Vehicle Refueling Emissions

Vehicle refueling emissions are attributable to vapor displaced from the automobile tank by dispensed gasoline and to spillage.

The two basic refueling vapor control alternatives are: control systems on service station equipment (Stage II controls), and control systems on vehicles (onboard controls). Onboard controls are basically limited to the carbon canister.

There are currently three types of Stage II systems in limited use in the United States: the vapor balance, the hybrid, and the vacuum assist systems. In the vapor balance system, gasoline vapor in the automobile fuel tank is displaced by the incoming liquid gasoline and is prevented from escaping to the atmosphere at the fillneck/nozzle interface by a flexible rubber “boot.” This boot is fitted over the standard nozzle and is attached to a hose similar to the liquid hose. The hose is connected to piping which vents to the underground tank. An exchange is made (vapor for liquid) as the liquid displaces vapor to the underground storage

tank. The underground storage tank assists this transaction by drawing in a volume of vapor equal to the volume of liquid removed.¹⁶⁰

The vacuum assist system differs from the balance system in that a “blower” (a vacuum pump) is used to provide an extra pull at the nozzle/fillneck interface. Assist systems can recover vapors effectively without a tight seal at the nozzle/fillpipe interface because only a close fit is necessary. A slight vacuum is maintained at the nozzle/fillneck interface allowing air to be drawn into the system and not allowing the vapors to escape. Because of this assist, the interface “boot” need not be as tight fitting as with balance systems. Further, the vast majority of assist nozzles do not require interlock mechanisms. Assist systems generally have vapor passage valves located in the vapor passage somewhere other than in the nozzles, resulting in a nozzle which is less bulky and cumbersome than nozzles employed by vapor balance systems.¹⁶⁰

There are four assist systems that are currently available and certified by the California Air Resources Board (CARB): the Hasstech, the Healy, the Hirt, and the Amoco Bellowless Nozzle System.¹⁶³

The hybrid system borrows from the concepts of both the balance and vacuum assist systems. It is designed to enhance vapor recovery at the nozzle/fillneck interface by vacuum, while keeping the vacuum low enough so that a minimum level of excess vapor/air is returned to the underground storage tank.

With the hybrid system, a small amount of the liquid gasoline (less than 10 percent) pumped from the storage tank is routed (before metering) to a restricting nozzle called an aspirator. As the gasoline goes through this restricting nozzle, a small vacuum is generated. This vacuum is used to draw vapors into the rubber boot at the interface. Because the vacuum is so small, very little excess air, if any, is drawn into the boot, hose and underground storage tank, and thus there is no need for a secondary processor, such as the vacuum assist's incinerator.¹⁵³

Results of the California Air Resources Board certification testing program on Stage II vapor recovery systems indicate that all of the Stage II vapor recovery systems discussed above are capable of achieving an emission reduction of 95 percent.¹⁶⁰ However, efficiencies vary depending upon inspection frequency, maintenance, and number of stations exempted. Reference 163 discusses efficiency in more detail.

Onboard vapor control systems consist of carbon canisters installed on the vehicle to control refueling emissions. The carbon canister system adsorbs, on activated carbon, the vapors which are displaced from the vehicle fuel tank by the incoming gasoline. Such a system first absorbs the emissions released during refueling and subsequently purges these vapors from the carbon to the engine carburetor when it is operating. This system is essentially an expansion of the present evaporative emissions control system used in all new cars to minimize breathing losses from the fuel tank and to control carburetor evaporative emissions. However, unlike the present system, a refueling vapor recovery system will require a tight seal at the nozzle/fillneck interface during refueling operations to ensure vapors flow into the carbon canister and are not lost to the atmosphere. An efficiency of 98 percent has been reported for control of automobile refueling losses using onboard control systems.¹⁶⁰

For additional information on control of vehicle refueling emissions at gasoline dispensing facilities refer to Reference 163.

6.4.8 Regulatory Analysis

Gasoline loading emissions at bulk gasoline terminals are regulated by the New Source Performance Standards promulgated on August 18, 1983.¹⁶⁶ These standards apply to VOC emissions at affected facilities that commenced construction or modification after December 17, 1980. The standards regulate bulk gasoline terminals with a throughput greater than 75,700 liters per day.

Also, the NESHAP for gasoline distribution that was promulgated on December 14, 1994, regulates organic hazardous air pollutant (HAP) emissions (including benzene) from gasoline loading and transport operations. The NESHAP covers HAP emissions from storage vessels, piping and handling, and loading at bulk gasoline terminals, and storage vessels at piping systems that handle the gasoline at pipeline breakout stations.¹⁶⁷

6.5 PUBLICLY OWNED TREATMENT WORKS

Publicly owned treatment works (POTWs) treat wastewater from residential, institutional, commercial, and industrial facilities. In general, benzene emissions from POTWs originate from the benzene content of industrial wastewater that is introduced into POTWs, and benzene may be emitted by volatilization at the liquid surface of the wastewater.

Industrial wastewater sent to POTWs from industrial facilities may be pre-treated or untreated, depending on State and Federal industrial wastewater quality standards. The following discussion describes the various treatment process units at POTWs from which benzene may be emitted.

6.5.1 Process Description of POTWs

A POTW treats wastewater using physical, chemical, and biological treatment processes. Most POTWs are required by Federal and State laws to treat wastewater using “primary” treatment methods to remove coarse and suspended solids and “secondary” treatment methods to remove biodegradable organics, pathogens, and additional solids. Additionally, some POTWs are required to use “tertiary” treatment methods to remove refractory organics, nutrients (e.g., phosphorus and nitrogen), dissolved inorganic salts, and heavy metals, among other contaminants. As the wastewater is treated, all of the collected solids and sludge undergo additional processing at the POTW to reduce sludge volume, organic content, and bacterial activity prior to disposal.

The following discussion describes the various process units included in a typical POTW facility (shown in Figure 6-6), that uses primary and secondary wastewater treatment methods.¹⁶⁸ As discussed in Section 6.6.2, a testing program for organic emissions from POTWs documented that benzene is emitted from most of these process units.

Comminutors

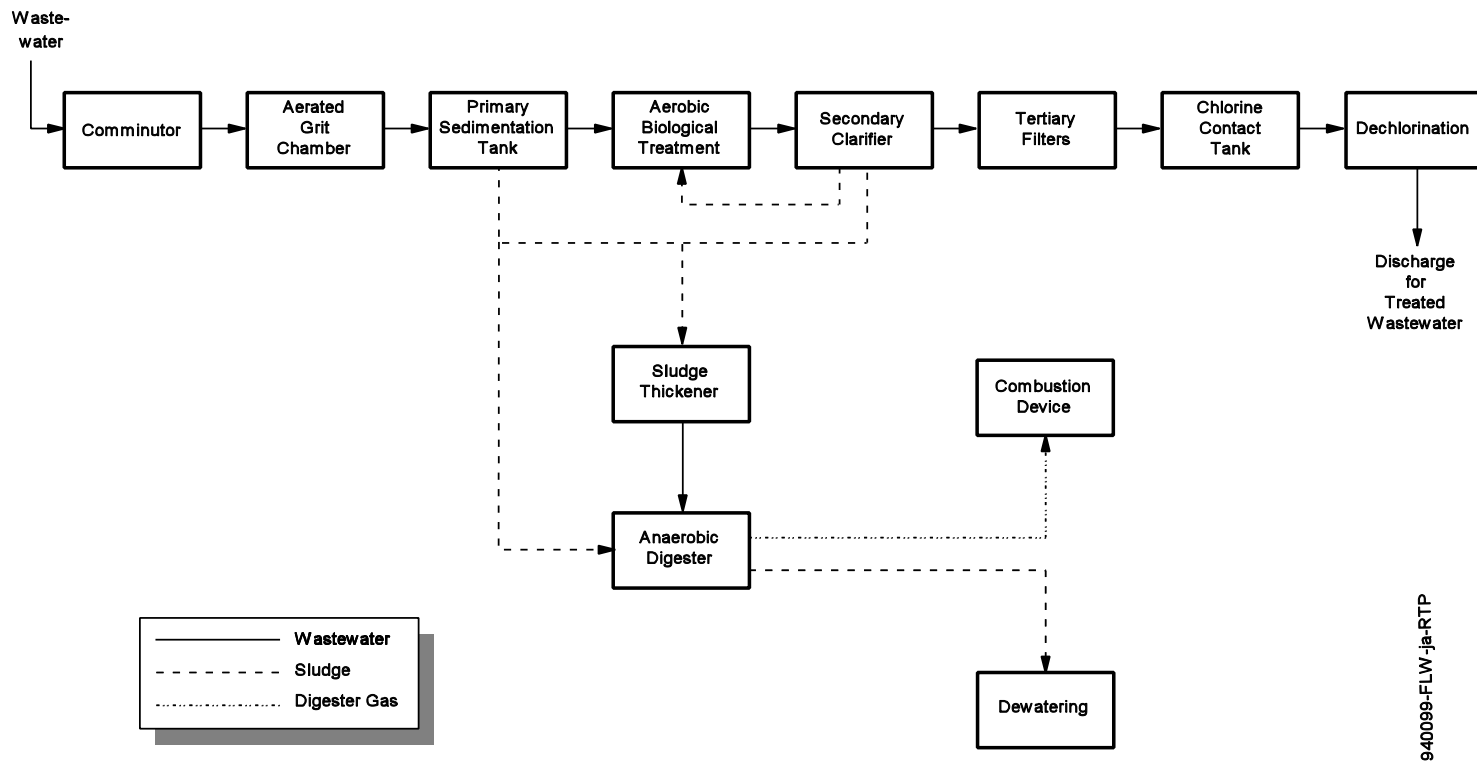
Comminutors (or shredders) are devices that are used to grind or cut waste solids to about one-quarter-inch (6 mm) particles. In one common type of comminutor, the untreated wastewater enters a slotted cylinder within which another similar cylinder with sharp-edged slots rotates rapidly. As the solids are reduced in size, they pass through the slots of the cylinders and move on with the liquid to the treatment plant. Comminution eliminates the need to use screens, which collect large solid waste material that must be disposed of separately from the sludge.¹⁶⁹

Aerated Grit Chambers

Grit chambers are used at many POTWs to remove dense solids (both inorganic and organic) present in wastewater (e.g., sand, gravel, glass, coffee grounds). Aerated grit chambers work by imparting a helical flow pattern to the sewage by aerating one side of the chamber. The aeration allows the dense grit to settle while keeping less dense organic material in suspension. Benzene emissions arise from aeration of the wastewater in the grit chamber.¹⁶⁸

Primary Sedimentation Tanks

The main function of primary sedimentation tanks is to remove suspended material that settles readily from raw sewage. This material includes slower-settling organic matter as well as fast-settling grit if the POTW does not have grit removal upstream. Additionally, the system removes floatable solids, which are composed mostly of fats and grease. The wastewater enters the tank at one end, flows through the tank and under a surface



940099-FLW-ja-RTP

Figure 6-6. Process Flow Diagram for a Typical POTW

Source: Reference 168.

baffle located near the tank's downstream edge, over a weir, and into an effluent channel. Sludge collects on the bottom of the tank. A system of scrapers collects the sludge from the bottom of the tank and pumps it to gravity sludge thickeners for further treatment. The surface baffle skims the surface of the water and collects the floatables for removal and treatment in anaerobic digesters.

Small amounts of benzene are released by volatilization from the quiescent section of the tank prior to the weir. Most of the benzene emissions from the primary sedimentation tank result from the turbulence that the water undergoes dropping over the weir into the outlet conveyance channel. The height of the water drop from the weir is a measure of the energy dissipated and may relate to the release of benzene emissions.¹⁶⁸

Aerobic Biological Treatments

Aerobic biological treatment involves the use of microorganisms to metabolize dissolved and colloidal organic matter in the wastewater in an aerobic environment. Two types of processes are used: suspended-growth and attached-growth. The most common suspended-growth process used in POTWs is the activated sludge process; the most common attached-growth process is the trickling filter. These two types of processes are described below.¹⁶⁹

Activated Sludge Process--In the activated sludge process, a high concentration of microorganisms that have settled in the secondary clarifiers (called activated sludge) is added to settled wastewater that enters an aerobic tank. The mixture enters an aeration tank, where the organisms and wastewater undergo further mixing with a large quantity of air or oxygen to maintain an aerobic environment. There are three common types of aeration tanks: diffused air, mechanically mixed air, and pure oxygen (which can be diffused or mechanically mixed). Diffused air systems aerate the water by bubbling air from the atmosphere through the water from the bottom of the tank. Mechanically mixed air systems use mechanical surface mixers that float on the water surface.

In pure oxygen systems (which are more likely to be covered systems), pure oxygen is fed to either submerged diffusers or to the head space over a tank employing mechanical aerators. In diffused air or oxygen systems, the air or oxygen bubbles can strip VOC from the liquid phase depending on the concentrations and partial pressures of the specific substances. In mechanically mixed systems, the area where the wastewater/activated sludge mixture is agitated is a potential source of VOC (benzene) emissions.^{168,169}

Trickling Filter--The trickling filter is an aerobic attached-growth treatment process that uses microorganisms growing on a solid media to metabolize organic compounds in the wastewater. Trickling filter media beds are typically 40 to 100 ft in diameter and 15 to 40 ft deep. Influent wastewater from the primary sedimentation tank is sprayed on top of the media bed. The wastewater is biologically treated as it trickles downward through the media. Effluent from the process is collected by the underdrain system and sent to a secondary clarifier. Ambient air is blown upward through the media to provide oxygen to sustain microbial growth. The exhaust air from the process may contain benzene that was stripped from the wastewater during treatment.¹⁶⁸

Secondary Clarification

Secondary clarification is a gravity sedimentation process used in wastewater treatment to separate out the activated sludge solids from the effluent from the upstream biotreatment process. Effluent from the biological treatment process is introduced into the clarifier through submerged diffusers. As the wastewater flows through the clarifier tank from inlet to outlet weirs, the solids settle to the bottom of the tank while the floatables and scum are skimmed off the top. The tank bottom is sloped slightly to the discharge end of the tank to two hoppers, where sludge is collected by a chain and flight conveyor system and returned to the biological treatment system or to the waste sludge handling system. The quiescent section of the tank may release benzene by volatilization from the water surface. However, most of the benzene emissions from the secondary clarifier result from the turbulence that the water undergoes dropping over the weir into the outlet conveyance channel. In some cases, the weir

is notched, such that the water flows through the notches, falling only a few inches onto a support structure. In this latter case, there is much less turbulence in the water, and it is expected that there would be fewer emissions of VOC than in the case where the water free-falls directly into the collection channel.¹⁶⁸

Tertiary Filters

Tertiary filters remove unsettled particles from the wastewater by using enclosed (pressure) filters or open (gravity) filters. The filtering medium typically consists of sand and anthracite coal, and may consist of one or two grain sizes. To collect activated sludge effluent, the filters typically remove particles in the size ranges of 3 to 5 μm and 80 to 90 μm . Alum or polymer is often added prior to filtration to form a floc and thus increase particulate removal.

Cleaning of tertiary filters (called backwashing) typically occurs by forcing water back through the filter. The backwash water is typically recirculated upstream in the plant. Except for the brief periods during backwash, gravity tertiary filters have quiescent surfaces, and little VOC release would be expected. Pressure filters are totally enclosed, and no air emissions occur during filtration from these units.¹⁶⁸

Chlorine Contact Tanks

For the purposes of disinfection, chlorine in the form of chlorine gas or calcium or sodium hypochlorite is fed into the wastewater just prior to the chlorine contact tank. The chlorine contact tank is designed to allow the mixture of chlorine and wastewater to remain in contact long enough to adequately kill the target organisms (15 minutes to 2 hours). The typical flow pattern is a serpentine pattern, consisting of interior baffle walls within a rectangular tank. Although water surfaces are generally quiescent, most chlorine contact tanks have weirs at the end of the tank to control water levels in the tank. Depending on the depth of fall and flow rate, the turbulence at the weir overflow may result in benzene emissions.¹⁶⁸

Dechlorination Chambers

Typically, a dechlorination chamber is located adjacent to the chlorine contact tank to remove chlorine residual in the disinfected wastewater. Chlorinated effluent from the chlorine contact tank flows into the dechlorination chamber through a gate valve. In the dechlorination chamber, an SO₂ solution or sodium bisulfate is introduced into the wastewater through submerged diffusers. The wastewater is hydraulically mixed as the SO₂ is added. The dechlorinated water is discharged from the facility.¹⁶⁸

Sludge Thickeners

Sludge thickeners collect primary sludge (from the primary sedimentation tank) and waste-activated sludge (from the secondary clarifier) to reduce the volume of the sludge prior to treatment in an anaerobic digester. The two most common types of thickening processes are gravity sludge thickeners and dissolved air floatation thickeners. These two types of thickeners are described below.¹⁶⁸ Additionally, centrifuges are used to thicken sludge both prior to and after aerobic digestion. (Centrifuges are discussed below under dewatering techniques.)

Gravity Sludge Thickener--In this process, sludge is thickened by allowing heavier sludge particles to settle. Sludge is pumped into the center of a circular tank from below. Heavier solid particles sink to the bottom of the tank, are removed as thickened sludge, and are sent to digesters. Lighter sludge particles (e.g., greases) float to the surface of the tank and are removed into a scum trough, where they are directed to a scum conditioner. As sludge is added to the tank, the sludge flows outward radially, and liquid effluent from the process flows outward over weirs and into the effluent trough located on the periphery of the tank. Typically, this liquid returns to the aeration tanks in the activated sludge process for further treatment.¹⁶⁸

Dissolved Air Flotation Thickener--This process is used to float sludge by forcing the sludge to rise to the water surface. Sludge is pumped into a circular tank with central feed or into a rectangular tank with end feed. As the sludge enters the tank, microbubbles are introduced into the sludge by pressurizing in a retention tank a portion of the effluent liquid from the tank. Pressurization of the liquid causes the air to be dissolved in the liquid phase. After pressurization, the recirculated effluent is mixed with the sludge feed. When the pressurized liquid is released to atmospheric pressure, the dissolved air is released into the solution in the form of microbubbles. As the sludge and pressurized liquid mix, the sludge and air mixture rises to the surface in the form of a sludge blanket. Sludge thickening occurs as a result of the sludge blanket and by drainage of entrained water from the sludge blanket. Surface skimmers are used to remove the sludge blanket from the water surface for further treatment in an anaerobic digester.

Anaerobic Digestion

Anaerobic digestion is a biological process conducted in the absence of free oxygen in which anaerobic and facultative bacteria metabolize organic solids in sludge, releasing methane and CO₂ as a by-product. Anaerobic digesters are most commonly cylindrical, with a diameter of 20 to 125 ft and a depth of 20 to 40 ft. In most digesters, to promote adequate contact between the anaerobic biota and organic matter, the sludge is mixed by either internal gas recirculation or by digested sludge recirculation. Additionally, the sludge is kept heated to about 95°F (35°C) by either direct steam injection into the sludge or by recirculating sludge through an external heat exchanging device. With mixing and heating, sludge undergoes digestion for about 15 to 25 days.^{168,169}

Most digesters are closed containers under a slight pressure. Under normal operation, there should be no direct emissions of benzene to the atmosphere. The digester gas produced is typically collected and routed to internal combustion engines to produce steam or generate electricity. (Refer to Section 7.5 for information about benzene emissions from an

internal combustion engine fueled with POTW digester gas.) If the digester is not covered or the digester gases are not collected, then benzene may be emitted directly from the digester.¹⁶⁸

Dewatering Techniques

Sludge dewatering operations involve removal of water from sludges by gravity, compression, and evaporation processes. Common methods of dewatering are using a belt filter press, a sludge centrifuge, and sludge drying beds.

Belt Filter Press--Digested sludge is mixed with flocculating cationic polymers which aid in the separation of the solids from the water. The flocculated sludge is initially spread out horizontally over a moving filter belt that passes under plows that turn the sludge/polymer solution, aiding in the dewatering process. After gravity thickening on the belt, the partially dewatered sludge is conveyed to and falls into a vertical compression zone, where water is squeezed out of the sludge between two filter belts moving concurrently through a series of rollers. The filtrate from dewatering is collected and returned to the head of the treatment plant for processing. Sludge particles enmeshed in the polyester belt fabric are continuously washed off by a highly pressurized spray. The dried sludge ("cake") product is collected and carried to silos for storage.

Benzene emissions from the belt filter press process may be released from the following locations: (1) the gravity section, where liquid sludge is discharged and tilled by plows, (2) the filtrate pans, where filtrate cascades down from the belts to the filtrate collection channel below, (3) the compression zone, where the sludge is squeezed between the two belts, and (4) the drainage sump into which the filtrate and wash water are discharged.¹⁶⁸

Sludge Centrifuge--Digested or pre-digested sludge mixed with flocculating cationic polymers is introduced into a spinning cylinder with a conical end bowl that rotates at sufficient velocity to force the solids to the sides of the drum. Inside the bowl, a concentric screw conveyor with helical flights turns at a slightly different speed than the rotating drum,

forcing the dewatered solids to a discharge at one end of the centrifuge, while the liquid flows over to a weir into a discharge at the other end. The dewatered sludge is collected and stored.¹⁶⁸ Benzene emissions may be emitted from the point where the separated liquid flows over the weir and is discharged from the centrifuge.

Sludge Drying Bed--A certain volume of sludge is piped into shallow beds, where the sludge is allowed to dry by gravity settling, evaporation, and percolation. Some drying beds are equipped with a system for decanting the liquid from the drying bed or draining the liquid through a sand bed to a collection pipe. Due to factors such as rainfall, ambient temperature, wind speed, relative humidity, amount of sun, and the character of the sludge, the drying time varies from 30 to 60 days.¹⁶⁸ These same factors will likely affect the level of benzene emissions from the sludge drying beds.

6.5.2 Benzene Emissions From POTWs

Under a program called the Pooled Emission Estimation Program (PEEP), 21 POTW facilities in California were tested for emissions of benzene (among other VOC) from 18 types of process units commonly included in POTW wastewater treatment processes. With the exception of one type of process unit (comminutor controlled with wet scrubber), the emissions test data yielded uncontrolled benzene emission factors. On average, three facilities were tested for each type of process unit. The types of process units that were tested are discussed above in section 6.6.1, and include aerated processes (aerated grit chambers, three types of activated sludge units, trickling filters, and dissolved air floatation thickeners), gas handling processes (anaerobic digesters and digester gas combustion devices), quiescent basins (primary sedimentation tanks, secondary clarifiers, tertiary filters, chlorine contact tanks, dechlorination, and gravity thickeners), sludge facilities (belt filter press, sludge centrifuges, and sludge drying beds), and other processes (comminutors).

Based on the data collected by PEEP, emission factors could be developed for most of the above process steps in the form of pounds of benzene emitted per million gallons

of wastewater treated at a POTW. One type of process unit tested (mechanically-mixed activated sludge) did not yield air emissions of benzene above the detection limit in the tests performed; however, benzene was detected in the wastewater treated by the tested units. Additionally, a benzene emission factor for the dechlorination process unit could only be calculated in the form of pounds of benzene emitted per pound of benzene in the wastewater influent to the dechlorination chamber. Refer to Table 6-22 for a listing of the emission factors.^{3,168}

With one exception, all of the emission factors presented in Table 6-21 represent uncontrolled emissions of benzene. However, many facilities employ measures for odor control that may also reduce benzene emissions to the atmosphere (see discussion in Section 6.6.3). Most of the facilities tested under PEEP did employ odor control methods; however, benzene emissions after control were not measured.

6.5.3 Control Technologies for POTWs

In general, the only types of control devices and techniques found at POTWs are the scrubbers and covers used to improve the odor of the air released from the process units. Using the information provided by PEEP, it could be determined which process units commonly employ covers and scrubbers.

In many cases, aerated grit chambers are covered and vented to a scrubber. Primary sedimentation tanks are sometimes covered and vented to a scrubber; however, many of these units are uncovered. Activated sludge units may sometimes be completely covered and vented to a scrubber or partially covered and vented to the atmosphere. This practice is more common if a pure oxygen system is employed. Trickling filter units are sometimes covered and vented to a scrubber. Secondary clarifiers may be uncovered or partially covered over the weir discharge area with no vents. Tertiary filters are commonly uncovered.

TABLE 6-22. SUMMARY OF BENZENE EMISSION FACTORS FOR POTWs

SCC Number	Emission Source	Control Device	Emission Factor lb/million gal (kg/million liters) ^a	Emission Factor Rating
5-01-007-07	Comminutor	Wet scrubber	6.50×10^{-3} (7.79×10^{-4})	E
5-01-007-15	Aerated grit chamber	Uncontrolled	3.56×10^{-3} (4.27×10^{-4})	C
5-01-007-20	Primary sedimentation tank	Uncontrolled	5.50×10^{-4} (6.59×10^{-5})	C
5-01-007-31	Diffused air activated sludge	Uncontrolled	6.67×10^{-4} (7.99×10^{-5})	B
5-01-007-33	Pure oxygen activated sludge	Uncontrolled	3.80×10^{-6} (4.55×10^{-7})	B
5-01-007-34	Trickling filter	Uncontrolled	1.60×10^{-3} (1.92×10^{-4})	C
5-01-007-40	Secondary clarifier	Uncontrolled	1.40×10^{-4} (1.68×10^{-5})	C
5-01-007-50	Tertiary filter	Uncontrolled	4.00×10^{-6} (4.79×10^{-7})	B
5-01-007-60	Chlorine contact tank	Uncontrolled	1.39×10^{-4} (1.67×10^{-5})	E
5-01-007-61	Dechlorination	Uncontrolled	7.50×10^{-1} lb/lb (7.50×10^{-1} kg/kg) ^b	B
5-01-007-71	Gravity sludge thickener	Uncontrolled	2.09×10^{-4} (2.50×10^{-5})	B

(continued)

TABLE 6-22. CONTINUED

SCC Number	Emission Source	Control Device	Emission Factor lb/million gal (kg/million liters) ^a	Emission Factor Rating
5-01-007-72	Dissolved air floatation thickener	Uncontrolled	3.00×10^{-3} (3.59×10^{-4})	B
5-01-007-81	Anaerobic digester	Uncontrolled	3.08×10^{-1} (3.69×10^{-2})	B
5-01-007-91	Belt filter press	Uncontrolled	5.00×10^{-2} (5.99×10^{-3})	B
5-01-007-92	Sludge centrifuge	Uncontrolled	2.05×10^{-3} (2.46×10^{-4})	B
5-01-007-93	Sludge drying bed	Uncontrolled	2.80×10^{-3} (3.36×10^{-4})	B

Source: References 3 and 168.

^a Factors are expressed as lb (kg) of benzene emitted per million gal (million liters) of wastewater treated.

^b Factor is expressed as lb (kg) of benzene emitted per lb (kg) of benzene in the wastewater influent to the process unit (emission source).

Chlorine contact tanks are either uncovered or partially covered. Dechlorination units are often enclosed in a building that vents to a scrubber. Thickeners are commonly covered and sometimes vented to a scrubber. Anaerobic digesters are commonly closed under a slight pressure, and the gas is sent to an internal combustion engine or boiler to produce steam or electricity; however, some digesters may vent to the atmosphere. Belt filter presses are commonly enclosed in a building that vents to a scrubber. Sludge centrifuges are commonly enclosed and vented to a scrubber. Drying beds are most commonly uncovered.¹⁶⁸

6.5.4 Regulatory Analysis

At the present, there are no Federal regulations that apply directly to benzene air emissions from POTWs. However, two regulations indirectly apply: the HON and the Benzene Waste Operations NESHAP. Both of these apply directly to specific types of industrial facilities that may generate wastewater containing benzene. Both regulations stipulate that these facilities may comply with the treatment requirements by sending their wastewater to an off-site treatment plant. However, the off-site plant must remove or destroy the benzene in the wastewater to the level specified in the regulations. Further information on the regulation can be found in Section 4.5.4 of this document.

6.6 MUNICIPAL SOLID WASTE LANDFILLS

A municipal solid waste (MSW) landfill unit is a discrete area of land or an excavation that receives household waste, but is not a land application unit (i.e. for receiving sewage sludge), surface impoundment, injection well, or waste pile. An MSW landfill unit may also receive other types of wastes, such as commercial solid waste, nonhazardous sludge, and industrial solid waste. Benzene emissions from MSW landfills are expected to originate from the non-household sources of MSW. The types of waste potentially accepted by MSW landfills include:

- MSW;

- Household hazardous waste;
- Municipal sludge;
- Municipal waste combustion ash;
- Infectious waste;
- Waste tires;
- Industrial non-hazardous waste;
- Conditionally exempt small quantity generator hazardous waste;
- Construction and demolition waste;
- Agricultural wastes;
- Oil and gas wastes; and
- Mining wastes.

MSW management in the United States is dominated by disposal in landfills. Approximately 67 percent of solid waste is landfilled, 16 percent is incinerated, and 17 percent is recycled or composted. There were an estimated 5,345 active MSW landfills in the United States in 1992. In 1990, active landfills were receiving an estimated 130 million tons (118 million Mg) of waste annually, with 55 to 60 percent reported as household waste and 35 to 45 percent reported as commercial waste.¹⁷⁰

6.6.1 Process Description of MSW Landfills¹⁷⁰

There are three major designs for municipal landfills: the area method, the trench method, and the ramp method. They all utilize a three-step process, which includes spreading the waste, compacting the waste, and covering the waste with soil. The area fill method involves placing waste on the ground surface or landfill liner, spreading it in layers, and compacting it with heavy equipment. A daily soil cover is spread over the compacted waste. The trench method entails excavating trenches designed to receive a day's worth of

waste. The soil from the excavation is often used for cover material and wind breaks. The ramp method is typically employed on sloping land, where waste is spread and compacted in a manner similar to the area method; however, the cover material obtained is generally from the front of the working face of the filling operation. The trench and ramp methods are not commonly used, and are not the preferred methods when liners and leachate collection systems are utilized or required by law.

Modern landfill design often incorporates liners constructed of soil (e.g., recompact clay) or synthetics (e.g., high density polyethylene) or both to provide an impermeable barrier to leachate (i.e., water that has passed through the landfill) and gas migration from the landfill.

6.6.2 Benzene Emissions from MSW Landfills

The rate of benzene emissions from a landfill is governed by gas production and transport mechanisms. Production mechanisms involve the production of the emission constituent in its vapor phase through vaporization, biological decomposition, or chemical reaction. Transport mechanisms involve the transportation of benzene in its vapor phase to the surface of the landfill, through the air boundary layer above the landfill, and into the atmosphere. The three major transport mechanisms that enable transport of benzene in its vapor phase are diffusion, convection, and displacement.¹⁷⁰

Uncontrolled Benzene Emissions¹⁷⁰

Uncontrolled benzene emissions from a landfill may be estimated by utilizing the series of equations provided below. The three equations estimate the following three variables: (1) the uncontrolled methane generation rate, (2) the uncontrolled benzene emission rate (calculated based on the uncontrolled methane generation rate), and (3) the uncontrolled benzene mass emission rate (calculated based on the uncontrolled benzene emission rate). As

indicated, the second equation utilizes the product of the first equation, and the third equation utilizes the product of the second equation.

The uncontrolled CH₄ volumetric generation rate may be estimated for individual landfills by using a theoretical first-order kinetic model of CH₄ production developed by EPA. This model is known as the Landfill Air Emissions Estimation model, and it can be accessed from the EPA's Control Technology Center web site. The Landfill Air Emissions Estimation model equation is as follows:

$$Q_{CH_4} = L_o R (e^{-kc} - e^{-kt})$$

where:

Q_{CH_4}	=	Methane volumetric generation rate at time t, m ³ /yr
L_o	=	Methane generation potential, m ³ CH ₄ /Mg refuse
R	=	Average annual acceptance rate of degradable refuse during active life, Mg/yr
e	=	Base log, unitless
k	=	Methane generation rate constant, yr ⁻¹
c	=	Time since landfill closure, yrs (c = 0 for active landfills)
t	=	Time since the initial refuse placement, yrs

Site-specific landfill information is generally available for variables R, c, and t. When refuse acceptance rate information is scant or unknown, R can be determined by dividing the refuse in place by the age of the landfill. Also, nondegradable refuse should be subtracted from the mass of acceptance rate to prevent overestimation of CH₄ generation. The average annual acceptance rate should only be estimated by this method when there is inadequate information on the actual average acceptance rate.

Values for variables L_o and k must be estimated. Estimation of the potential CH₄ generation capacity of refuse (L_o) is generally treated as a function of the moisture and organic content of the refuse. Estimation of the CH₄ generation constant (k) is a function of a variety of factors, including moisture, pH, temperature, and other environmental factors, and

landfill operating conditions. Specific CH₄ generation constants can be computed by use of EPA Method 2E.

The Landfill Air Emission Estimation model uses the proposed regulatory (see Section 6.6.4) default values for L_o and k. However, the defaults were developed for regulatory compliance purposes. As a result, the model contains conservative L_o and k default values in order to protect human health, to encompass a wide range of landfills, and to encourage the use of site-specific data. Therefore, different L_o and k values may be appropriate in estimating landfill emissions for particular landfills and for use in an emissions inventory.

A higher k value of 0.05/yr is appropriate for areas with normal or above normal precipitation. An average k value is 0.04/yr. For landfills with drier waste, a k value of 0.02/yr is more appropriate. An L_o value of 125 m³/Mg (4,005 ft³/ton) refuse is appropriate for most landfills. It should be emphasized that in order to comply with the proposed regulation (see Section 6.6.4), the model defaults for k and L_o must be applied as specified in the final rule.

Based on the CH₄ volumetric generation rate calculated above, the benzene volumetric emission rate from a landfill can be estimated by the following equation:

$$Q_{BZ} = 2 Q_{CH_4} * C_{BZ} / (1 \times 10^6)$$

where:

Q _{BZ}	=	Benzene volumetric emission rate, m ³ /yr
Q _{CH₄}	=	CH ₄ volumetric generation rate, m ³ /yr (from the Landfill Air Emission Estimation model)
C _{BZ}	=	Benzene concentration in landfill gas, ppmv
2	=	Multiplication factor (assumes that approximately 50 percent of landfill gas is CH ₄)

Uncontrolled emission concentrations of benzene based on a landfill site's history of co-disposal with hazardous wastes are presented in Table 6-23.^{3,170} An analysis of

TABLE 6-23. SUMMARY OF UNCONTROLLED EMISSION CONCENTRATIONS OF
BENZENE FROM LANDFILLS

SCC Number	Emission Source	Type of Waste Disposed	Emission Concentration (ppmv)	Emission Factor Rating
5-02-006-02	Landfill dump	MSW co-disposed with hazardous waste	24.99	D
		MSW, unknown history of co-disposal with hazardous waste	2.25	B
		MSW only	0.37	D

Source: References 3 and 170.

benzene emissions data based on the co-disposal history of the individual landfills from which the concentration data were derived indicates that benzene emissions do vary with the amount of hazardous waste co-disposed. These benzene concentrations have already been corrected for air infiltration and can be used, when site-specific data are not available, as input parameters (for the variable C_{BZ}) in the above equation for estimating benzene volumetric emission rates from landfills.

Then, based on the benzene volumetric emission rate calculated using the above equation, the uncontrolled mass emission rate of benzene from a landfill can be estimated by the following equation:

$$I_{BZ} = Q_{BZ} * \frac{78.113}{(8.205 \times 10^{-5} \text{ m}^3\text{-atm/mol-}^\circ\text{K}) (1000 \text{ g}) (273 + T)}$$

where:

I_{BZ}	=	Uncontrolled benzene mass emission rate, kg/yr
Q_{BZ}	=	Benzene volumetric emission rate, m ³ /yr
T	=	Temperature of landfill gas, °C
78.113	=	Molecular weight of benzene

This equation assumes that the operating pressure of the system is approximately 1 atmosphere. If the temperature of the landfill gas is not known, a temperature of 25°C is recommended.

Controlled Benzene Emissions

As discussed in more detail in Section 6.6.3, emissions from landfills are typically controlled by installing a gas collection system and destroying the collected gas through the use of internal combustion engines, flares, or turbines. The control system for landfills consists of two stages, and estimating controlled benzene emissions involves the following two steps: (1) estimating the amount of benzene that is not collected by the gas collection system, and (2) estimating the amount of collected benzene that is not destroyed by the control device.

The amount of benzene that is not collected by the gas collection system may be calculated with the following equation:

$$UC_{BZ} = \left(1 - \frac{\text{Collection Efficiency}}{100} \right) * I_{BZ}$$

where:

UC_{BZ}	=	Uncollected benzene mass emission rate, kg/yr
Collection Efficiency	=	Collection efficiency of the gas collection system, %
I_{BZ}	=	Uncontrolled benzene mass emission rate, kg/yr

If the site-specific collection efficiency cannot be determined, one may assume that a gas collection system collects 75 percent of the benzene emitted by a landfill. Reported collection efficiencies typically range from 60 to 85 percent, with the average of 75 percent being most commonly used for estimation of UC_{BZ} .

The amount of benzene that is not destroyed by the control device may be calculated with the following equation:

$$ND_{BZ} = \left(1 - \frac{\text{Destruction Efficiency}}{100} \right) * (I_{BZ} - UC_{BZ})$$

where:

ND_{BZ}	=	Non-destroyed benzene mass emission rate, kg/yr
Destruction Efficiency	=	Destruction efficiency of the control device, %
I_{BZ}	=	Uncontrolled benzene mass emission rate, kg/yr
UC_{BZ}	=	Uncollected benzene mass emissions rate, kg/yr

If the site-specific destruction efficiency of a control device cannot be determined, one may assume the destruction efficiencies provided here. Flares have been documented to destroy

89.5 percent of the benzene routed to the flare. Internal combustion engines have been documented to destroy 83.8 percent of the benzene routed to the internal combustion engine. After promulgation of standards proposed in 1991 (see Section 6.6.4), however, all control devices utilized at both new and existing landfills may be required to reduce the non-methanogenic organic compounds (NMOCs) in the collected gas by 98 weight percent.

Alternatively, if the control device utilized is a flare and the heat content of the landfill gas is known, the emission factor provided in Table 6-24 may be used to calculate non-destroyed benzene emissions.³ Additionally, if the control device is an industrial boiler, refer to Section 7.4 for information regarding controlling benzene emissions from an industrial boiler treating landfill gas.

After UC_{BZ} and ND_{BZ} have been calculated, these two variables may be added together to calculate the total benzene mass emission rate after the control system.

6.6.3 Control Technologies for MSW Landfills¹⁷⁰

Landfill gas collection systems are either active or passive systems. Active collection systems provide a pressure gradient in order to extract landfill gas by use of mechanical blowers or compressors. Passive systems allow the natural pressure gradient created by the increase in landfill pressure from landfill gas generation to mobilize the gas for collection.

Landfill gas control and treatment options include (1) combustion of the landfill gas, and (2) purification of the landfill gas. Combustion techniques include techniques that do not recover energy (e.g., flares and thermal incinerators) and techniques that recover energy and generate electricity from the combustion of the landfill gas (e.g., gas turbines and internal combustion engines). Boilers can also be employed to recover energy from landfill gas in the form of steam. Flares involve an open combustion process that requires oxygen for combustion; the flares can be open or enclosed. Thermal incinerators heat an organic chemical

TABLE 6-24. CONTROLLED BENZENE EMISSION FACTOR FOR LANDFILLS

SCC Number	Emission Source	Control Device	Emission Factor lb/MMBtu (g/kJ) ^a	Emission Factor Rating
5-02-006-01	Landfill Dump	Flare	7.10x10 ⁻⁶ (3.05x10 ⁻⁹) ^b	D

Source: Reference 3.

^a Emission factor is in lb (g) of benzene emitted per MMBtu (kJ) of heat input to the flare.

^b Based on two tests conducted at two landfill sites.

to a high enough temperature in the presence of sufficient oxygen to oxidize the chemical to CO₂ and water. Purification techniques can also be used to process raw landfill gas to pipeline quality natural gas by using adsorption, absorption, and membranes.

6.6.4 Regulatory Analysis¹⁷⁰

Proposed NSPS and emission guidelines for air emissions from MSW landfills for certain new and existing landfills were published in the Federal Register on May 30, 1991, and promulgated March 12, 1996. The regulation requires that Best Demonstrated Technology be used to reduce MSW landfill emissions from affected new and existing MSW landfills with a design capacity greater than 2.8 million tons (2.5 million Mg by mass or 2.5 million cubic meters by volume) of MSW and emitting greater than or equal to 55 tons/yr (50 Mg/yr) of NMOCs. The MSW landfills that would be affected by the proposed NSPS would be each new MSW landfill and each existing MSW landfill that has accepted waste since May 30, 1991, or that has capacity available for future use. Control systems would require (1) a well-designed and well-operated gas collection system, and (2) a control device capable of reducing NMOCs in the collected gas by 98 weight percent.

6.7 PULP, PAPER, AND PAPERBOARD INDUSTRY

In the pulp, paper, and paperboard industry, wood pulp is chemically treated by dissolving the lignin that binds the cellulose together and then extracting the cellulose to make paper and paperboard. Four types of chemical wood pulping processes are practiced in the

United States. Kraft pulping is the most prevalent type of process, accounting for about 85 percent of pulp production. Three other pulping processes, semi-chemical, soda-mill, and acid sulfite, account for 4, 5, and 6 percent of domestic pulp production, respectively. Because kraft pulping is the most common type of pulping and the other processes are relatively similar to it, kraft pulping will be the focus of this section. More information on the other three pulping processes can be found in References 171 and 172.

The distribution of kraft pulp mills in the United States in 1993 is shown in Table 6-25.¹⁷¹ Kraft pulp mills are located primarily in the southeast, whose forests provide over 60 percent of U.S. pulpwood.

The U.S. EPA is developing benzene emission factors for pulp and papermaking processes in conjunction with MACT standards that are under development. Please refer to the CHIEF web site for benzene emission factors that will be forthcoming from the MACT development process. More information on the MACT effort is given in Section 6.7.2.

6.7.1 Process Description for Pulp, Paper, and Paperboard Making Processes

The key unit operations in the kraft pulp and papermaking process include: (1) cooking and evaporation, (2) pressure knotting and screening, (3) brown stock washing, (4) decker washing and screening, (5) oxygen delignification, (6) pulp storage, (7) chemical recovery and causticizing, (8) co-product recovery, (9) bleaching, and (10) paper making. Common potential emission points found in the pulp and papermaking process are listed in Table 6-26.¹⁷³ Each of the key steps, along with their associated emission points, are illustrated in the diagram of a typical Kraft pulping and recovery process (Figure 6-7) and these are discussed below in more detail.¹⁷¹ Bleaching, which is frequently used as a final step, and papermaking are discussed at the end of this section.

TABLE 6-25. DISTRIBUTION OF KRAFT PULP MILLS IN THE
UNITED STATES (1993)

State	Kraft Pulp Mills
Alabama	16
Arizona	1
Arkansas	7
California	4
Florida	8
Georgia	12
Idaho	1
Kentucky	2
Louisiana	10
Maine	7
Maryland	1
Michigan	3
Minnesota	2
Mississippi	6
Montana	1
New Hampshire	1
North Carolina	5
Ohio	1
Oklahoma	1
Oregon	7
Pennsylvania	3
South Carolina	6
Tennessee	2
Texas	6
Virginia	4
Washington	7
Wisconsin	4
Total	126

Source: Reference 171.

TABLE 6-26. LIST OF COMMON POTENTIAL EMISSION POINTS WITHIN THE KRAFT PULP AND PAPERMAKING PROCESS

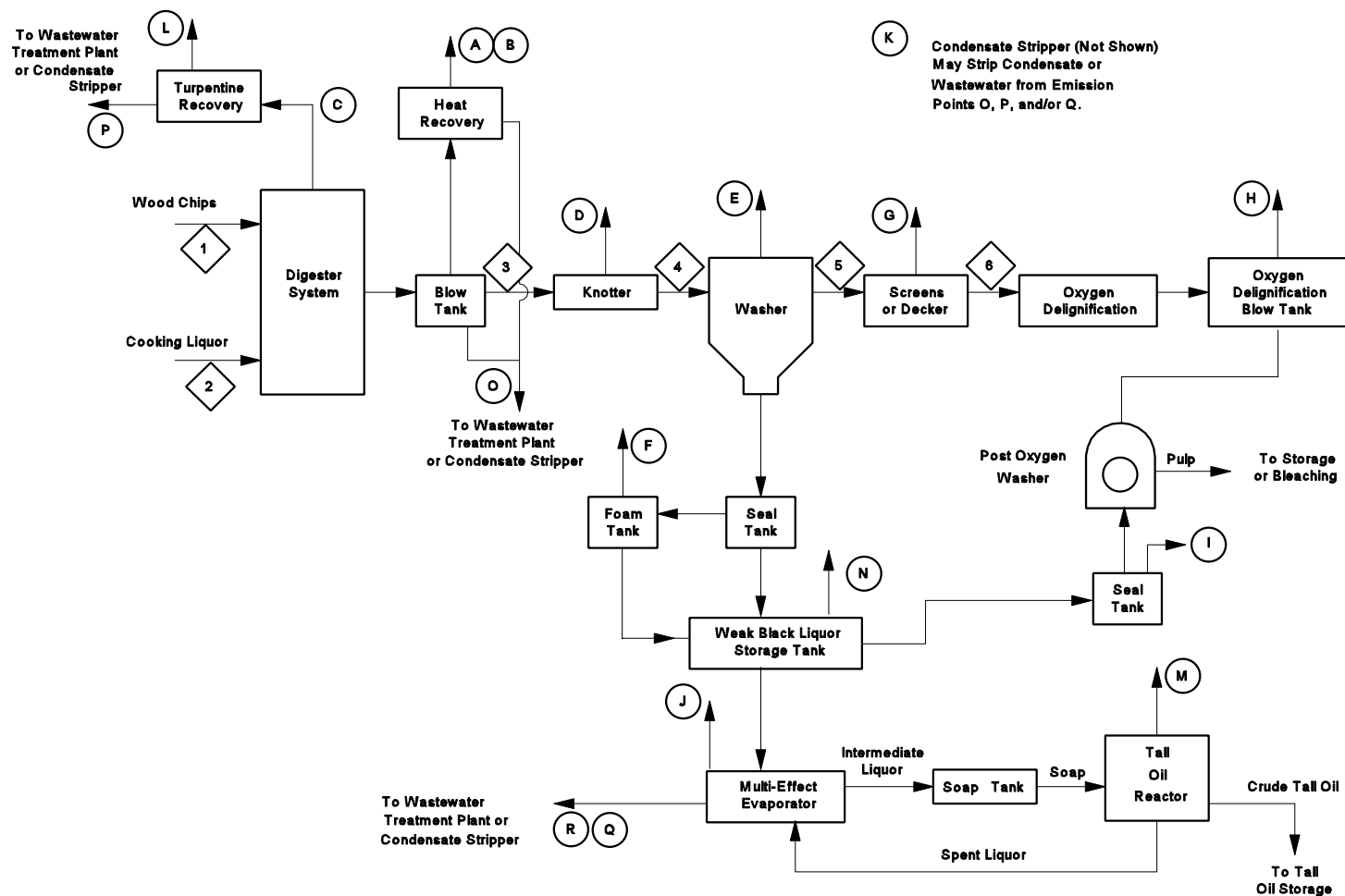
Digester relief vents	Washer filtrate tanks
Turpentine recovery system vents	Decker
Digester blow gas vents	Screen
Noncondensable gas system vents	Weak black liquor storage tank
Evaporator noncondensable gas vent	Recovery furnace stack
Evaporator hotwell gas vent	Slaker/causticizer vents
Knotter	Lime kiln stack
Brownstock or pulp washer	Bleach plant vents
Washer foam tanks	Papermachine vents

Source: Reference 173.

Cooking and Evaporation

The pulping or cooking process begins with the digester, which is a pressure vessel that is used to chemically treat chips and other cellulosic fibrous materials (such as straw, bagasse, rags, etc.) under elevated temperature and pressure to separate fibers from each other. This digestion process frequently takes place in an aqueous chemical solution (frequently a white liquor solution of sodium hydroxide and sodium sulfide). The digestion process may be batch or continuous. After cooking the liquor containing the cooking chemicals and lignin is separated from the pulp and sent to a series of evaporators for concentration.

The entire digester and black liquor evaporator system includes (a) the outlet to the incinerator for the low-volume-high-concentration (LVHC) gases that are commonly collected and routed to such an incineration device, (b) chip bin exhaust vents, and (c) other miscellaneous digester and evaporator system emission points. These systems were combined since all kraft mills collect and incinerate digester relief gases (Vent C), digester blow tank and accumulator gases (Vent A [continuous] and Vent B [batch process]), and evaporator



840043-FLW-ja-RTP

Figure 6-7. Typical Kraft Pulp-making Process with Chemical Recovery

Source: Reference 171.

condenser vents (Vent J). The gases at these emission points are assumed to be routed to the combustion device and the benzene reduced by 98 percent.¹⁷¹

Deknotting and Prewash Screening

The pulp from the blow tank enters a knotter where knots (pieces of undigested wood) are removed prior to pulp washing in order to produce a higher-quality chemical pulp (Emission Point D).¹⁷¹ The pressure knotter and pre-washer screening system includes all the equipment following the digester system (i.e., post blow tank) and preceding the first stage of brown stock washing. There are two types of knotters typically used in the industry, open and pressurized. The air flow across the two types varies. Open knotters have a greater flow and, therefore, are expected to have higher emissions than pressurized knotters. Knotter systems typically include equipment such as knot drainer hoods, knot tanks, knot elevators, and screened stock chests. Not every piece of equipment is necessarily vented to the atmosphere (Emission Point D). The emission factor presented is based on the assumption of a pressurized knotter and pre-washing screening system.

Brown Stock Wash

Pulp that has been through the blow tank and knotter is then washed with water in the brownstock washing process. The purpose of washing is to remove black liquor from the pulp so as to recover the cooking chemicals sodium and sulfur and to avoid contamination during subsequent processing steps. The brown stock washing system includes all the brown stock washers, associated filtrate tanks, vacuum pump exhausts, and any interstage storage chests that follow pre-washer screening. In washing, water (fresh or recycled) is used to rinse the pulp and recover the black liquor. There are two basic types of brown stock washing systems, the rotary vacuum drum system and the more advanced pressure or diffusion washers. Emissions from the washing process occur as compounds entrained in the pulp and black liquor slurry volatilize (Emission Point E).

The diluted or “weak” black liquor is recovered in a washer filtrate tank and sent to the evaporator area. A washer foam tank is typically used to capture the foam separated in the filtrate tank. Foam is formed when soap, which is dissolved by the caustic cooking liquors, goes through the washing process. In general, defoaming is completed in the foam tank using centrifugal or mechanical force to break up the foamed mass. This force allows air trapped in the foam mass to vent to the atmosphere from the washer foam tank (Emission Point F). The defoamed weak black liquor is routed to a weak black liquor storage tank (Emission Point N) before it is typically piped to the evaporator area.¹⁷¹

Screening and Decking

Screening is performed to remove oversized particles from the pulp slurry after washing the pulp and prior to the papermaking process. The decker is a washing and thickening unit that follows brown stock washing and precedes oxygen delignification (if present), bleaching (if present), or the paper machines. The decker unit is assumed to consist of a drum and a filtrate tank, both of which are assumed to be vented to the atmosphere. The emissions from each part of this decker unit (i.e., both the washer and the filtrate tank) fall within the range of emissions reported for individually tested decker washers and decker filtrate tanks and is therefore assumed to be representative.

Decker vents may be either hooded (an open space above the decker with a hood covering the unit) or well-enclosed (tightly fitted hood around the unit, no open space except through the hood). Hooded deckers are likely to have a much greater air flow across the decker, and therefore are expected to have greater emissions (Emission Point G).

Oxygen Delignification

Following the screening and/or decking, delignification of pulp with oxygen (called oxygen delignification) prior to bleaching is sometimes used. By removing more of the

lignin from the pulp, this pretreatment step helps to reduce the amount of chemicals used by the bleach plant.

The oxygen delignification (OD) system begins with the oxygen reactor and associated blow tank (Emission Point H). This system includes a series of two washers and/or presses following the oxygen reactor blow tank, each with a filtrate tank. An interstage storage chest located between the first and second washers and/or presses is also a common configuration.

Pulp Storage Tank

Pulp storage tanks refers to the large bulk storage tanks following OD (if present) or brown stock washers that store the pulp that is to be routed to the bleach plant or to the paper machines. One pulp storage tank is assumed to be present for each pulping line.

Chemical Recovery and Causticizing

The chemical recovery and causticizing area of the mill is where strong black liquor recovered from the evaporators and concentrators is converted into white liquor for reuse in the digesters. This system includes all the equipment associated with chemical recovery, beginning with the recovery furnace, the smelt dissolving tanks and ending with the white liquor clarifier.

The chemical recovery and causticizing area is an example of a mill system where the number of pieces of equipment tested was driving the emissions. In other words, if one mill tested all the components of the recovery loop, that mill would show higher emissions for the causticizing area system. The causticizing area system can be broken down into the following subsystems:

Recovery furnace. Strong black liquor from the multiple effect evaporators is concentrated from 50 to about 70 percent solids either in a concentrator or in a direct contact evaporator before being fired in a recovery furnace. The organics in the liquor provide the energy required to both make steam and to capture the inorganic chemicals as smelt at the bottom of the furnace.

Smelt dissolving tank. Smelt from the recovery furnace is fed into the tank where it is dissolved by weak wash. Smelt dissolving tanks are typically equipped with a venturi scrubber for particulate control. Weak wash from the lime mud washer is often used as the make-up solution in the scrubber, with spent scrubbing solution flowing into the dissolving tank.

Green liquor clarifier. Effluent from the smelt dissolving tank (green liquor) enters a clarifier. Dregs are drained off the bottom of the clarifier, and the clarified green liquor passes on to a slaker.

Slaker and causticizers. Green liquor from the green liquor clarifier is converted into white liquor by adding lime in the slaker and causticizers. Emissions from the causticizers and the slaker are typically routed to a common venturi scrubber with green liquor or fresh mill water as the scrubbing medium.

White liquor clarifier. White liquor is clarified and the clarified white liquor is sent to storage. The bottoms from the white liquor clarifier (lime mud) are sent to a mud washer.

Lime mud washer system. Lime mud from the white liquor clarifier is washed here with fresh mill water. The wash water effluent from the mud washer is termed weak wash which is used in the smelt dissolving tank. The lime mud washer system includes the actual washer plus all associated equipment such as dilution tanks, pressure filters, and mix

tanks. If condensates are used as the wash water, the emissions could be much higher, depending on the quality of the condensates.

Lime kiln. The lime kiln accepts washed lime mud and calcines it to produce lime. This lime in turn is fed to the slaker, and the cycle is repeated. The lime kiln is typically equipped with a venturi scrubber using fresh mill water as the scrubbing medium for particulate emission control. Alternatively, particulates may be controlled by an electrostatic precipitator (ESP).

Co-product Recovery

Turpentine and soap (tall oil) are two saleable coproducts that may be byproducts of the pulping process. Turpentine is recovered from digester relief gases when resinous softwoods such as pines are pulped. In general, the digester relief gases are vented to a condenser to reduce the gas moisture content and to a cyclone separator to remove any small wood chips or fines. Emissions are generated as turpentine and water and are separated in a decanter. These emissions are released through the turpentine recovery system vent. Tall oils are recovered in a reactor, but emissions are expected to be low because the weak black liquor has already been stripped of volatiles in the evaporation process (Vent M).¹⁷¹

Bleaching

Bleaching is the process of further delignifying and whitening pulp by chemically treating it to alter the coloring matter and to impart a higher brightness.

To enhance the physical and optical qualities (whiteness and brightness) of the pulp, one of two types of chemical bleaching is used. The first type of bleaching, called brightening, uses selective chemicals (such as hydrogen peroxide) that destroy chromatographic groups but do not materially attack the lignin. Brightening produces a product with a temporary brightness (such as newspaper). In the second type (true bleaching),

oxidizing chemicals (such as chlorine, chlorine dioxide, and sodium hypochlorite) are used to remove residual lignin, resulting in a high-quality, stable paper pulp.¹⁷¹

The most common bleaching and brightening agents are chlorine, chlorine dioxide, hydrogen peroxide, oxygen, caustic (sodium hydroxide) and sodium hypochlorite. Typically, the pulp is treated with each chemical in a separate stage. One example stage which illustrates the use of one bleaching agent is shown in Figure 6-8.¹⁷¹ Each stage includes a tower where the bleaching occurs (Vent A). The washer (Vent B) removes the bleaching chemicals and dissolved lignins from the pulp prior to entering the next stage. The seal tank (Vent C) collects the washer effluent to be used as wash water in other stages or to be sewered (Vent D).¹⁷¹

Paper Machine

Paper machine emissions include all the emissions from the various pieces of equipment following pulp storage and/or bleaching that are used to turn the pulp into a finished paper product. The data show that the factor driving emissions from paper machines is paper type (i.e., unbleached versus bleached).

Wastewater/Condensate Treatment

In addition to process vents, emissions also occur from the treatment of wastewater or condensates generated during the making of pulp and paper (Emission Point O).¹⁷¹

6.7.2 Benzene Emissions from Pulp, Paper and Papermaking Processes

EPA published MACT standards for the pulp, paperboard, and papermaking industry on April 15, 1998.¹⁷³ While the supporting documentation for these standards does not specifically call out benzene as a major pollutant from pulp and paper mills, it

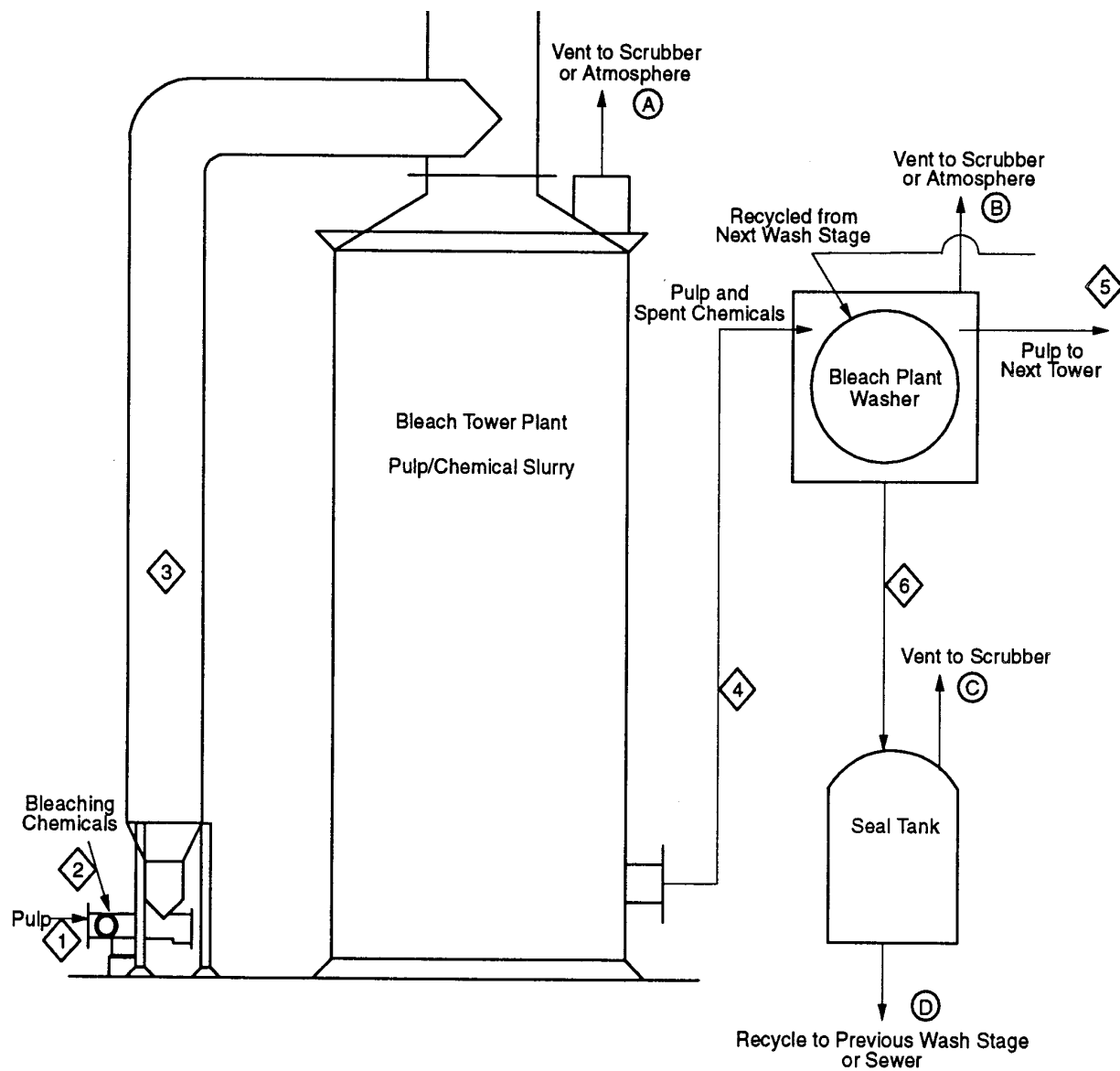


Figure 6-8. Typical Down-flow Bleach Tower and Washer

Source: Reference 171.

does mention benzene as being emitted from this source and as a pollutant that would be affected by VOC reductions achieved by compliance with the standards.

Emission points may include the digester relief vents, digester blow gas vents, brownstock or pulp washer, screen, as well as bleaching and brightening. Once washing has occurred, it is expected that benzene would be found in the wastewater, which is recycled for use throughout the process. Such uses of this recycled water include as a solvent for digesting chemicals, as the pulp digesting medium, as pulp waste water, and as a diluent for screening, cleaning, and subsequent pulp processing. Benzene emissions would then be expected from each step in the pulping process where this recycled wastewater is used. Note that the extent of benzene emissions (as with any HAP) during the pulping process is a function of the level of pulp production, type of digestion (batch or continuous), and the type of wood pulped.

6.8 SYNTHETIC GRAPHITE MANUFACTURING

Synthetic graphite is a composite of coke aggregate (filler particles), petroleum pitch (binder carbon), and pores (generally with a porosity of 20 to 30 percent). Synthetic graphite is a highly refractory material that has been thermally stabilized to as high as 5,400°F (3,000°C). Graphite is a valuable structural material because it has high resistance to thermal shock, does not melt, and possesses structural strength at temperatures well above the melting point of most metals and alloys. Applications for synthetic graphite include the following industries: aerospace (e.g., nose cones, motor cases, and thermal insulation), chemical (e.g., heat exchangers and centrifugal pumps and electrolytic anodes for the production of chlorine and aluminum), electrical (e.g., telephone equipment products, electrodes in fuel cells and batteries, and contacts for circuit breakers and relays), metallurgical (e.g., electric furnace electrodes for the production of iron and steel, furnace linings, ingot molds, and extrusion dies), nuclear (e.g., moderators, thermal columns, and fuel elements), and miscellaneous (e.g., motion picture projector carbons).¹⁷⁴

The number of facilities manufacturing synthetic graphite in the United States was not identified.

6.8.1 Process Description for Synthetic Graphite Production

Synthetic graphite is produced from calcined petroleum coke and coal tar pitch through a series of processes including crushing, sizing, mixing, cooling, extruding, baking, pitch impregnation, rebaking, and graphitization. Throughout the process of thermal conversion of organic materials to graphite, the natural chemical driving forces cause the growth of larger and larger fused-ring aromatic systems, and ultimately result in the formation of the stable hexagonal carbon network of graphite. A process flow diagram of the synthetic graphite manufacturing process is provided in Figure 6-9.^{174,175}

Calcined petroleum coke (i.e., raw coke that has been heated to temperatures above 2,200°F (1,200°C) to remove volatiles and shrink the coke to produce a strong, dense particle) is crushed and screened to obtain uniform-sized fractions for the formulation of dry ingredient. Coal tar pitch is stored in heated storage tanks and is pumped to the mixing process, as needed, as the liquid ingredient. The dry ingredient is weighed and loaded, along with a metered amount of coal tar pitch, into a heated mixing cylinder (heated to at least 320°F [160°C]), where they are mixed until they form a homogeneous mixture. During the mixing process, vapors (Vent A in Figure 6-9) are ducted to a stack where they are discharged to the atmosphere.^{174,175}

The heated mixture is sent to a cooling cylinder which rotates, cooling the mixture with the aid of cooling fans to a temperature slightly above the softening point of the binder pitch. Vapors from the cooling process (Vent B in Figure 6-9) are often vented to a PM control device before being vented to the atmosphere.^{174,175}

The cooled mixture is charged to a hydraulic press, then pressed through a die to give the mixture the desired shape and size. The extruded mixture is referred to as “green